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<p>(21) International Application Number: PCT/US94/08947 (22) International Filing Date: 9 August 1994 (09.08.94) (30) Priority Data: 08/113,495 27 August 1993 (27.08.93) US (71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Protector & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventor: OFOSU-ASANTE, Kofi; 1209 Brushwood, Cincinnati, OH 45224 (US). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).</p>		<p>(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ, GE, HU, JP, KG, KP, KR, KZ, LK, LT, LV, MD, MG, MN, NO, NZ, PL, RO, RU, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD). Published <i>With international search report Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: CONCENTRATED LIQUID OR GEL DISHWASHING DETERGENT COMPOSITIONS CONTAINING CALCIUM IONS AND DISULFONATE SURFACTANTS (57) Abstract Concentrated liquid or gel dishwashing detergent compositions containing high active levels of surfactant, calcium ions and disulfonate surfactant are disclosed. The compositions exhibit improved stability as well as providing good cleaning and grease removal benefits. Particularly preferred compositions also contain simple sugars.</p>		

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CONCENTRATED LIQUID OR GEL DISHWASHING DETERGENT COMPOSITIONS
CONTAINING CALCIUM IONS AND DISULFONATE SURFACTANTS

TECHNICAL FIELD

The present invention relates to stable concentrated liquid or gel dishwashing detergent compositions containing high active levels of detergent surfactant, calcium ions, and disulfonate surfactants.

BACKGROUND OF THE INVENTION

Typical light duty liquid or gel dishwashing detergents contain from about 15% to about 30% anionic surfactant. Formulation of concentrated detergent compositions are becoming ever more popular, especially in the laundry and automatic dishwashing detergent compositions. These concentrated compositions address many environmental concerns by reducing the amount of packing and product material needed and/or used. Additionally, light duty liquid or gel dishwashing detergents with good grease removal benefits are much desired by consumers. Calcium and magnesium ions have been added to certain liquid or gel detergent compositions to improve grease cleaning benefits. However, it is often difficult to formulate a stable concentrated liquid or gel dishwashing detergent composition containing calcium ions from typical ion sources such as calcium chloride and/or calcium formate.

It has been surprisingly found that a stable calcium containing concentrated liquid or gel detergent composition can be formed by the addition of from about 0.1% to about 40% disulfonate surfactants. The disulfonate surfactant not only improves product stability but also enhances grease cleaning, acts as a hydrotrope and is highly stable in both acid and hydrogen peroxide environments.

SUMMARY OF THE INVENTION

A liquid or gel dishwashing detergent composition comprising, by weight:

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(a) from about 20% to about 95% of a surfactant selected from the group consisting of anionic surfactants, nonionic surfactants, amphoteric surfactants and mixtures thereof;

(b) from about 0.01% to about 4.0% of calcium ions;

5 (c) from about 0.1% to about 40% disulfonate surfactant; and

(d) from about 5% to about 45% water;

wherein said composition has a pH in a 10% solution in water at 20°C of between from about 7 and about 10.

A particularly preferred embodiment also comprises from about
10 0.1% to about 5.0% by weight simple sugars.

DETAILED DESCRIPTION OF THE INVENTION

The concentrated liquid or gel, preferably liquid, dishwashing detergent compositions of the present invention
15 contain a surfactant, a source of calcium ions and disulfonate surfactant. The compositions herein may also contain a simple sugar for additional stability benefits. These and other complementary optional ingredients typically found in liquid or gel dishwashing compositions are set forth below.

20 The term "light duty dishwashing detergent composition" as used herein refers to those compositions which are employed in manual (i.e. hand) dishwashing.

The term "concentrated" as used herein refers to a detergent composition containing at least 40% total surfactant.

25 By the term "sugar" is meant a mono- or di- saccharide or a derivative thereof, or a degraded starch or chemically modified degraded starch which is water soluble.

Surfactants

The compositions of this invention comprise from about 20% to
30 about 95%, preferably from about 30% to about 75%, more preferably from about 40% to about 70% by weight anionic surfactant, nonionic surfactant, amphoteric surfactant, and mixtures thereof. These surfactants contribute foaming, detergency, and/or mildness to the composition.

35 Included in this category are several anionic surfactants commonly used in liquid or gel dishwashing detergents. The cations associated with these anionic surfactants can be alkali

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metal, ammonium, mono, di-, and tri-ethanolammonium, preferably sodium, potassium ammonium and mixtures thereof. Examples of anionic co-surfactants that are useful in the present invention are the following classes:

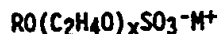
5 (1) Alkyl benzene sulfonates in which the alkyl group contains from 9 to 15 carbon atoms, preferably 11 to 14 carbon atoms in straight chain or branched chain configuration. An especially preferred linear alkyl benzene sulfonate contains about 12 carbon atoms. U.S. Pat. Nos. 2,220,099 and 2,477,383 describe
10 these surfactants in detail.

(2) Alkyl sulfates obtained by sulfating an alcohol having 8 to 22 carbon atoms, preferably 12 to 16 carbon atoms. The alkyl sulfates have the formula $ROS_3^-M^+$ where R is the C₈-22 alkyl group and M is a mono- and/or divalent cation.

15 (3) Paraffin sulfonates having 8 to 22 carbon atoms, preferably 12 to 16 carbon atoms, in the alkyl moiety. These surfactants are commercially available as Hostapur SAS from Hoechst Celanese.

(4) Olefin sulfonates having 8 to 22 carbon atoms, preferably 12 to 16 carbon atoms. U.S. Pat. No. 3,332,880
20 contains a description of suitable olefin sulfonates.

(5) Alkyl ether sulfates derived from ethoxylating an alcohol having 8 to 22 carbon atoms, preferably 12 to 16 carbon atoms, less than 30, preferably less than 12, moles of ethylene oxide. The alkyl ether sulfates having the formula:
25



where R is a C₈-22 alkyl group, x is 1-30, and M is a mono- or divalent cation.

(6) Alkyl glyceryl ether sulfonates having 8 to 22 carbon atoms, preferably 12 to 16 carbon atoms, in the alkyl moiety.
30

(7) Fatty acid ester sulfonates of the formula:



wherein R₁ is straight or branched alkyl from about C₈ to C₁₈, preferably C₁₂ to C₁₆, and R₂ is straight or branched alkyl from about C₁ to C₆, preferably primarily C₁, and M⁺ represents a mono-
35 or divalent cation.

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(8) Secondary alcohol sulfates having 6 to 18, preferably 8 to 16 carbon atoms.

(9) The following general structures illustrate some of the special soaps (or their precursor acids) employed in this invention.

- 5 A. A highly preferred class of soaps used herein comprises the C₁₀-C₁₆ secondary carboxyl materials of the formula R³CH(R⁴)COOM, wherein R³ is CH₃(CH₂)_x and R⁴ is CH₃(CH₂)_y, wherein y can be 0 or an integer from 1 to 6, x is an integer from 6 to 12 and the sum of (x + y) is 6-12, preferably 7-11, most preferably 8-9.
- 10 B. Another class of special soaps useful herein comprises those carboxyl compounds wherein the carboxyl substituent is on a ring hydrocarbyl unit, i.e., secondary soaps of the formula R⁵-R⁶-COOM, wherein R⁵ is C₇-C₁₀, preferably C₈-C₉, alkyl or alkenyl and R⁶ is a ring structure, such as benzene, cyclopentane, cyclohexane, and the like. (Note: R⁵ can be in the ortho, meta or para position relative to the carboxyl on the ring.)
- 15 C. Still another class of soaps includes the C₁₀-C₁₈ primary and secondary carboxyl compounds of the formula R⁷CH(R⁸)COOM, wherein the sum of the carbons in R⁷ and R⁸ is 8-16, R⁷ is of the form CH₃-(CHR⁹)_x and R⁸ is of the form H-(CHR⁹)_y, where x and y are integers in the range 0-15 and R⁹ is H or a C₁-4 linear or branched alkyl group. R⁹ can be any combination of H and C₁-4 linear or branched alkyl group members within a single -(CHR⁹)_{x,y} group; however, each molecule in this class must contain at least one R⁹ that is not H. These types
- 20 of molecules can be made by numerous methods, e.g. by hydroformylation and oxidation of branched olefins, hydroxycarboxylation of branched olefins, oxidation of the products of Guerbet reaction involving branched oxoalcohols. The branched olefins can be derived by oligomerization of shorter olefins, e.g. butene, isobutylene, branched hexene, propylene and pentene.
- 25
- 30
- 35

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5 D. Yet another class of soaps includes the C₁₀-C₁₈ tertiary carboxyl compounds, e.g., neo-acids, of the formula R¹⁰CR¹¹(R¹²)COOM, wherein the sum of the carbons in R¹⁰, R¹¹ and R¹² is 8-16. R¹⁰, R¹¹, and R¹² are of the form CH₃-(CHR¹³)_x, where x is an integer in the range 0-13, and R¹³ is H or a C₁₋₄ linear or branched alkyl group. Note that R¹³ can be any combination of H and C₁₋₄ linear or branched alkyl group members within a single
10 -(CHR¹³)_x group. These types of molecules result from addition of a carboxyl group to a branched olefin, e.g., by the Koch reaction. Commercial examples include the neodecanoic acid manufactured by Exxon, and the VersaticTM acids manufactured by Shell.

15 In each of the above formulas A, B, C and D, the species M can be any suitable, especially water-solubilizing, counterion, e.g., H, alkali metal, alkaline earth metal, ammonium, alkanolammonium, di- and tri- alkanolammonium, C₁-C₅ alkyl substituted ammonium and the like. Sodium is convenient, as is diethanolammonium.

20 Preferred secondary soaps for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid; 2-pentyl-1-heptanoic acid; 2-methyl-1-dodecanoic acid; 2-ethyl-1-undecanoic acid; 2-propyl-1-decanoic acid; 2-butyl-1-nonanoic acid;
25 2-pentyl-1-octanoic acid and mixtures thereof.

(10) Mixtures thereof.

30 The above described anionic surfactants are all available commercially. It should be noted that although both dialkyl sulfosuccinates and fatty acid ester sulfonates will function well at neutral to slightly alkaline pH, they will not be chemically stable in a composition with pH much greater than about 8.5. It should also be noted that sulfate impurities may be present due to hydrolysis of alkyl sulfates, alkyl ether sulfates or reaction of
35 trapped SO₃ from the sulfation or sulfonation process with water. The sulfate contaminant may be detrimental with respect to stability of the product. It is therefore an important

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consideration that the anionic surfactant used in this embodiment contain very low levels (i.e. less than 1%, preferably from 0 to about 0.6%, more preferably from 0 to about 0.3% by weight), if any, sulfate ion impurity.

5 Suitable nonionic detergent surfactants are generally disclosed in U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, at column 13, line 14 through column 16, line 6, incorporated herein by reference. Exemplary, non-limiting classes of useful nonionic surfactants are listed below.

10 1. The polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols. In general, the polyethylene oxide condensates are preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from 6 to 12 carbon atoms in either a straight- or
15 branched-chain configuration with the alkylene oxide. Commercially available nonionic surfactants of this type include IgepalTM CO-630, marketed by the GAF Corporation; and TritonTM X-45, X-114, X-100, and X-102, all marketed by the Rohm & Haas Company.

20 2. The condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 8 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols
25 having an alkyl group containing from about 10 to about 20 carbon atoms with from about 2 to about 10 moles of ethylene oxide per mole of alcohol.

30 3. The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of these compounds preferably has a molecular weight of from about 1500 to about 1800 and exhibits water insolubility.

35 4. The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine.

5. Alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group

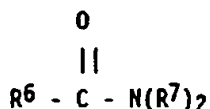
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containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. U.S. Patent Nos. 4,373,203 and 4,732,704, incorporated herein by reference, also describe acceptable surfactants.

These surfactants are typically present at a concentration of from about 1% to about 15%, preferably from about 2% to about 10% by weight.

6. Alkyl ethoxy carboxylate of the present invention is of the generic formula $RO(CH_2CH_2O)_xCH_2COO-M^+$ wherein R is a C_{12} to C_{16} alkyl group, x ranges from 0 to about 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than about 20%, preferably less than about 15%, most preferably less than about 10%, and the amount of material where x is greater than 7 is less than about 25%, preferably less than about 15%, most preferably less than about 10%, the average x is from about 2 to 4 when the average R is C_{13} or less, and the average x is from about 3 to 6 when the average R is greater than C_{13} , and M is a cation, preferably chosen from alkali metal, ammonium, mono-, di-, and tri-ethanolammonium, most preferably from sodium, potassium, ammonium, and mixtures thereof with magnesium ions. The preferred alkyl ethoxy carboxylates are those where R is a C_{12} to C_{14} alkyl group. Suitable processes for preparing the alkyl ethoxy carboxylates are disclosed in U.S. Patent No. 5,233,087, incorporated herein by reference.

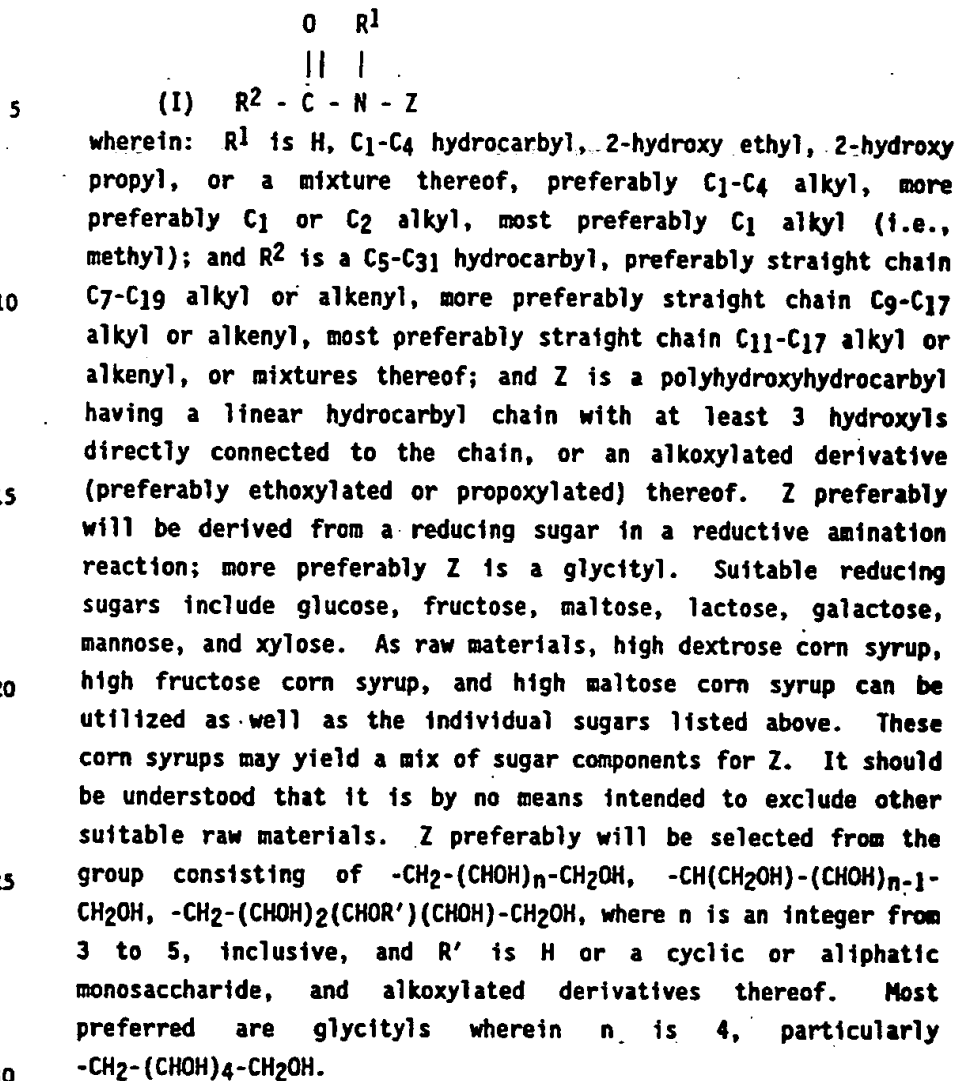
Other surfactants include fatty acid amide surfactants having the formula:



wherein R^6 is an alkyl group containing from 7 to 21, preferably from 9 to 17, carbon atoms and each R^7 is selected from the group consisting of hydrogen, C_1 - C_4 alkyl, C_1 - C_4 hydroxyalkyl, and $-(C_2H_4O)_xH$ where x varies from about 1 to about 3.

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The compositions hereof may also contain a polyhydroxy fatty acid amide surfactant of the structural formula:



In Formula (I), R^1 can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl.

35 $\text{R}^2-\text{CO}-\text{N}<$ can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

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Z can be 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl, 1-deoxymannityl, 1-deoxymalto-
triotityl, etc.

5 Methods for making polyhydroxy fatty acid amides are known in the art. In general, they can be made by reacting an alkyl amine with a reducing sugar in a reductive amination reaction to form a corresponding N-alkyl polyhydroxyamine, and then reacting the N-alkyl polyhydroxyamine with a fatty aliphatic ester or triglyceride in a condensation/amidation step to form the N-alkyl, N-polyhydroxy fatty acid amide product. Processes for making
10 compositions containing polyhydroxy fatty acid amides are disclosed, for example, in G.B. Patent Specification 809,060, published February 18, 1959, by Thomas Hedley & Co., Ltd., U.S. Patent 2,965,576, issued December 20, 1960 to E. R. Wilson, and U.S. Patent 2,703,798, Anthony M. Schwartz, issued March 8, 1955,
15 and U.S. Patent 1,985,424, issued December 25, 1934 to Piggott, each of which is incorporated herein by reference.

In a preferred process for producing N-alkyl or N-hydroxyalkyl, N-deoxyglycityl fatty acid amides wherein the
20 glycityl component is derived from glucose and the N-alkyl or N-hydroxyalkyl functionality is N-methyl, N-ethyl, N-propyl, N-butyl, N-hydroxyethyl, or N-hydroxy-propyl, the product is made by reacting N-alkyl- or N-hydroxyalkyl-glucamine with a fatty ester selected from fatty methyl esters, fatty ethyl esters, and fatty triglycerides in the presence of a catalyst selected from
25 the group consisting of trilithium phosphate, trisodium phosphate, tripotassium phosphate, tetrasodium pyrophosphate, pentapotassium tripolyphosphate, lithium hydroxide, sodium hydroxide, potassium hydroxide, calcium hydroxide, lithium carbonate, sodium carbonate, potassium carbonate, disodium tartrate, dipotassium tartrate,
30 sodium potassium tartrate, trisodium citrate, tripotassium citrate, sodium basic silicates, potassium basic silicates, sodium basic aluminosilicates, and potassium basic aluminosilicates, and mixtures thereof. The amount of catalyst is preferably from about 0.5 mole % to about 50 mole %, more preferably from about 2.0 mole
35 % to about 10 mole %, on an N-alkyl or N-hydroxyalkyl-glucamine molar basis. The reaction is preferably carried out at from about

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138°C to about 170°C for typically from about 20 to about 90 minutes. When triglycerides are utilized in the reaction mixture as the fatty ester source, the reaction is also preferably carried out using from about 1 to about 10 weight % of a phase transfer agent, calculated on a weight percent basis of total reaction mixture, selected from saturated fatty alcohol polyethoxylates, alkylpolyglycosides, linear glycamide surfactant, and mixtures thereof.

Preferably, this process is carried out as follows:

- (a) preheating the fatty ester to about 138°C to about 170°C;
- (b) adding the N-alkyl or N-hydroxyalkyl glucamine to the heated fatty acid ester and mixing to the extent needed to form a two-phase liquid/liquid mixture;
- (c) mixing the catalyst into the reaction mixture; and
- (d) stirring for the specified reaction time.

Also preferably, from about 2% to about 20% of preformed linear N-alkyl/N-hydroxyalkyl, N-linear glucosyl fatty acid amide product is added to the reaction mixture, by weight of the reactants, as the phase transfer agent if the fatty ester is a triglyceride. This seeds the reaction, thereby increasing reaction rate.

These polyhydroxy "fatty acid" amide materials also offer the advantages to the detergent formulator that they can be prepared wholly or primarily from natural, renewable, non-petrochemical feedstocks and are degradable. They also exhibit low toxicity to aquatic life.

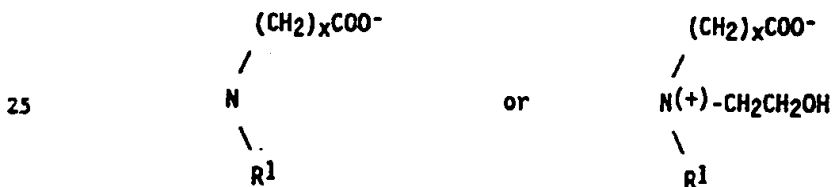
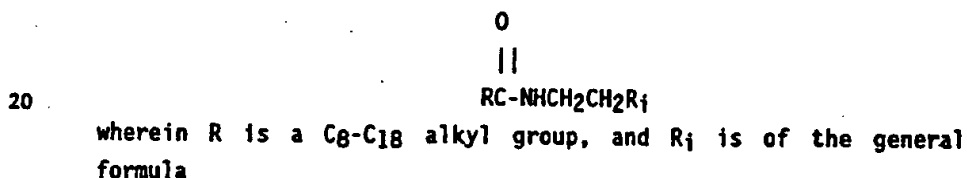
It should be recognized that along with the polyhydroxy fatty acid amides of Formula (I), the processes used to produce them will also typically produce quantities of nonvolatile by-product such as esteramides and cyclic polyhydroxy fatty acid amide. The level of these by-products will vary depending upon the particular reactants and process conditions. Preferably, the polyhydroxy fatty acid amide incorporated into the detergent compositions hereof will be provided in a form such that the polyhydroxy fatty acid amide-containing composition added to the detergent contains less than about 10%, preferably less than about 4%, of cyclic

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polyhydroxy fatty acid amide. The preferred processes described above are advantageous in that they can yield rather low levels of by-products, including such cyclic amide by-product.

Other ampholytic surfactants may also be incorporated into the detergent compositions hereof. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight-branched chains. One of the aliphatic substituents contains at least 8 carbon atoms, typically from 8 to 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975, at column 19, lines 18-35 (herein incorporated by reference) for examples of useful ampholytic surfactants.

Alkyl amphocarboxylic acids can be added of the generic formula:

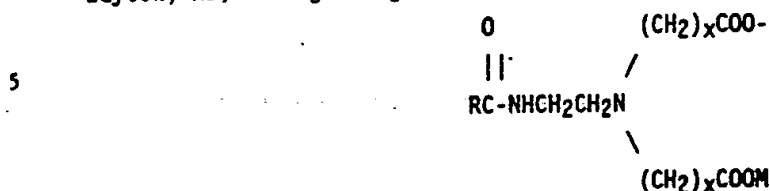


wherein R¹ is a (CH₂)_xCOOM or CH₂CH₂OH, and x is 1 or 2 and M is preferably chosen from alkali metal, alkaline earth metal, ammonium, mono-, di-, and tri-ethanolammonium, most preferably from sodium, potassium, ammonium, and mixtures thereof with magnesium ions. The preferred R alkyl chain length is a C₁₀ to C₁₄ alkyl group.

In a preferred embodiment, the amphocarboxylic acid is an amphodicarboxylic acid produced from fatty imidazolines wherein the dicarboxylic acid functionality of the amphodicarboxylic acid is diacetic acid and/or dipropionic acid. A suitable example of

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an alkyl amphodicarboxylic acid for use herein is the amphoteric surfactant Miranol® C2M Conc. manufactured by Miranol, Inc., Dayton, NJ, having the general formula:



wherein R is a C₈ to C₁₈ alkyl group, and x is 1 or 2, and M is a cation.

Zwitterionic surfactants may also be incorporated into the detergent compositions hereof. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975, at column 19, line 38 through column 22, line 48 (herein incorporated by reference) for examples of useful zwitterionic surfactants.

Such ampholytic and zwitterionic surfactants are generally used in combination with one or more anionic and/or nonionic surfactants.

If included in the compositions of the present invention, these additional surfactants are typically present at a concentration of from about 1% to about 15%, preferably from about 2% to about 10% by weight of the composition.

Calcium Ions

The presence of calcium ions greatly improves the cleaning of greasy soils for compositions of the present invention. This is especially true when the compositions are used in softened water that contains few divalent ions.

The calcium ions can be added to the composition in the following forms chloride, acetate, xylene sulfonate, formate or nitrate, preferably a chloride, xylene sulfonate and/or formate, salt to compositions of the present invention.

The calcium ions are present in the compositions hereof at a level of from about 0.01% to 4.0%, preferably from about 0.05% to

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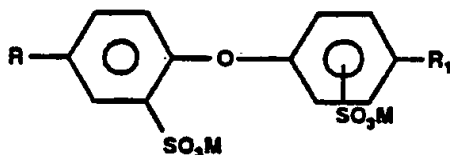
3.5%, more preferably from about 0.1% to about 2.0%, by weight of the composition.

The amount of calcium ions present in compositions of the invention will be dependent upon the total amount of anionic and/or nonionic surfactant. When calcium ions and anionic and/or nonionic surfactants are present in the compositions of this invention, the molar ratio of calcium ions to total anionic and/or nonionic surfactant is from about 1:15 to about 1:2 for compositions of the invention.

Disulfonates

In the present invention from about 0.1% to about 40%, preferably from about 0.5% to about 25%, more preferably from about 1% to about 10% disulfonate surfactant can be present.

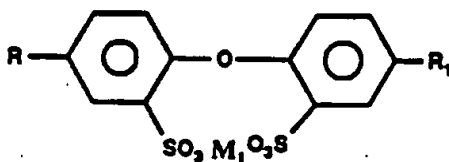
Suitable disulfonate surfactants include the alkyl diphenyl oxide disulfonate surfactants of the general formula:



R = C10-C18, may be branched or linear

R₁ = H or R

M = Na⁺, K⁺, NH₄⁺, CA⁺⁺, or Mg⁺⁺



R = C10-C18, may be branched or linear

R₁ = H or R

M¹ = CA⁺⁺ or Mg⁺⁺

Suitable commercially available disulfonate surfactants are the DOWFAX® series from Dow Chemical (Dowfax 2A1, 3B2, 8290) and the POLY-TERGENT® series from Olin Corp.

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Water

Compositions herein will typically contain up to about 45%, preferably from about 5% to about 45%, most preferably from about 20% to about 40%, of water.

5 pH of the Composition

The pH of the composition of the present invention in a 10% solution in water at 20°C is from about 7 to about 10, more preferably from about 7 to about 9.

10 Dishwashing compositions of the invention will be subjected to acidic stresses created by food soils when put to use, i.e., diluted and applied to soiled dishes. If a composition with a pH greater than 7 is to be most effective in improving performance, it should contain a buffering agent capable of maintaining the alkaline pH in the composition and in dilute solutions, i.e.,
15 about 0.1% to 0.4% by weight aqueous solution, of the composition.

The pKa value of the buffering agent should be about 0.5 to 1.0 pH units below the desired pH value of the composition (determined as described above). Preferably, the pKa value of the buffering agent should be between about 7 and about 9.5. Under
20 these conditions the buffering agent most effectively controls the pH while using the least amount thereof.

The buffering agent may be an active detergent in its own right, or it may be a low molecular weight, organic or inorganic material that is used in this composition solely for maintaining
25 an alkaline pH. Preferred buffering agents for compositions of this invention are nitrogen-containing materials. Some examples are amino acids or lower alcohol amines like mono-, di-, and tri-ethanolamine. Other preferred nitrogen-containing buffering agents are 2-amino-2-ethyl-1,3-propanediol, 2-amino-2-methyl-
30 propanol, 2-amino-2-methyl-1,3-propanediol, tris-(hydroxymethyl)-aminomethane (a.k.a. tris) and disodium glutamate. N-methyl diethanolamine, 1,3-diamino-2-propanol N,N'-tetramethyl-1,3-diamino-2-propanol, N,N-bis(2-hydroxyethyl)glycine (a.k.a. bicine), and N-tris (hydroxymethyl)methyl glycine (a.k.a. tricine)
35 are also preferred. Mixtures of any of the above are acceptable. The buffering agent is present in the compositions of the invention hereof at a level of from about 0.1% to 15%, preferably

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from about 1% to 10%, most preferably from about 2% to 8%, by weight of the composition.

Saccharide

5 The present invention comprises from about 0.1% to about 5.0%, preferably from about 0.5% to about 4.0% of a mono- or di-saccharide. The saccharide repeating unit can have as few as five carbon atoms or as many as fifty carbon atoms consistent with water solubility. The saccharide derivative can be an alcohol or acid of the saccharide. By "water-soluble" in the present context
10 it is meant that the sugar is capable of forming a clear solution or a stable colloidal dispersion in distilled water at room temperature at a concentration of 0.01 g/l.

Amongst the sugars which are useful in this invention are sucrose, which is most preferred for reasons of availability and cheapness, cellobiose, lactulose, maltose (malt sugar), and
15 lactose which are disaccharides. Useful mono-saccharide derivatives include gluconic acid, glucose, fructose, galactose, xylose, arabinose, and ribose.

Suds Booster

20 Another component which may be included in the composition of this invention is a suds stabilizing surfactant (suds booster) at a level of less than about 15%, preferably from about 0.5% to 12%, more preferably from about 1% to 10% by weight of the composition. Optional suds stabilizing surfactants operable in the instant
25 composition are: sultaines, complex betaines, betaines, ethylene oxide condensates, fatty acid amides, amine oxide semi-polar nonionics, and cationic surfactants.

The composition of this invention can contain betaine detergent surfactants having the general formula:



wherein R is a hydrophobic group selected from the group consisting of alkyl groups containing from about 10 to about 22 carbon atoms, preferably from about 12 to about 18 carbon atoms, alkyl aryl and aryl alkyl groups containing a similar number of
35 carbon atoms with a benzene ring being treated as equivalent to about 2 carbon atoms, and similar structures interrupted by amido or ether linkages; each R¹ is an alkyl group containing from 1 to

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about 3 carbon atoms; and R^2 is an alkylene group containing from 1 to about 6 carbon atoms.

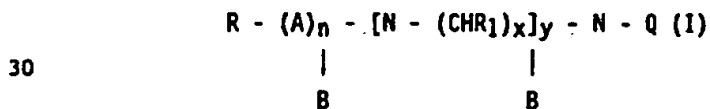
Examples of preferred betaines are dodecyl dimethyl betaine, cetyl dimethyl betaine, dodecyl amidopropyl dimethyl betaine, 5 tetradecyl dimethyl betaine, tetradecyl amidopropyl dimethyl betaine, and dodecyl dimethyl ammonium hexanoate.

Other suitable amidoalkyl betaines are disclosed in U.S. Pat. Nos. 3,950,417; 4,137,191; and 4,375,421; and British Patent GB No. 2,103,236, all of which are incorporated herein by reference.

10 It will be recognized that the alkyl (and acyl) groups for the above betaine surfactants can be derived from either natural or synthetic sources, e.g., they can be derived from naturally occurring fatty acids; olefins such as those prepared by Ziegler, or Oxo processes; or from olefins separated from petroleum either 15 with or without "cracking".

The sultaines useful in the present invention are those compounds having the formula $(R(R^1)_2N^+R^2SO_3^-)$ wherein R is a C_6 - C_{18} hydrocarbyl group, preferably a C_{10} - C_{16} alkyl group, more preferably a C_{12} - C_{13} alkyl group, each R^1 is typically C_1 - C_3 20 alkyl, preferably methyl, and R^2 is a C_1 - C_6 hydrocarbyl group, preferably a C_1 - C_3 alkylene or, preferably, hydroxyalkylene group. Examples of suitable sultaines include C_{12} - C_{14} dimethylammonio-2-hydroxypropyl sulfonate, C_{12} -14 amido propyl ammonio-2-hydroxypropyl sultaine, C_{12} -14 dihydroxyethylammonio 25 propane sulfonate, and C_{16} -18 dimethylammonio hexane sulfonate, with C_{12} -14 amido propyl ammonio-2-hydroxypropyl sultaine being preferred.

The complex betaines for use herein have the formula:

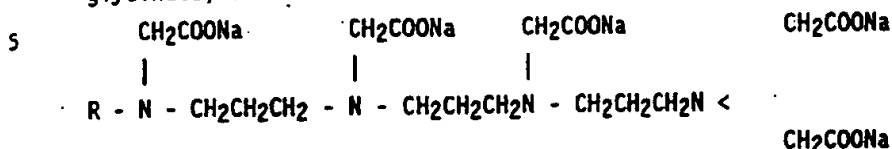


30 wherein R is a hydrocarbon group having from 7 to 22 carbon atoms, A is the group $C(O)$, n is 0 or 1, R_1 is hydrogen or a lower alkyl group, x is 2 or 3, y is an integer of 0 to 4, Q is the group 35 $-R_2COOM$ wherein R_2 is an alkylene group having from 1 to 6 carbon atoms and M is hydrogen or an ion from the groups alkali metals,

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alkaline earth metals, ammonium and substituted ammonium and B is hydrogen or a group Q as defined.

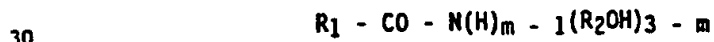
An example in this category is alkylamphopolycarboxy glycinate, of the formula:



The ethylene oxide condensates are broadly defined as compounds produced by the condensation of ethylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which can be aliphatic or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired balance between hydrophilic and hydrophobic elements.

Examples of such ethylene oxide condensates suitable as suds stabilizers are the condensation products of aliphatic alcohols with ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched and generally contains from about 8 to about 18, preferably from about 8 to about 14, carbon atoms for best performance as suds stabilizers, the ethylene oxide being present in amounts of from about 8 moles to about 30, preferably from about 8 to about 14 moles of ethylene oxide per mole of alcohol.

Examples of the amide surfactants useful herein include the ammonia, monoethanol, and diethanol amides of fatty acids having an acyl moiety containing from about 8 to about 18 carbon atoms and represented by the general formula:

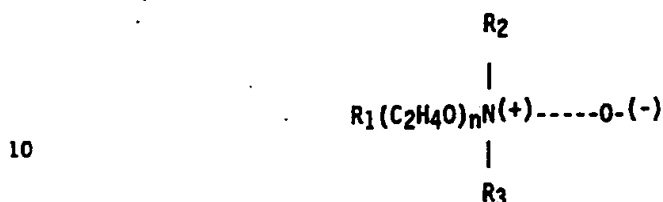


wherein R is a saturated or unsaturated, aliphatic hydrocarbon radical having from about 7 to 21, preferably from about 11 to 17 carbon atoms; R₂ represents a methylene or ethylene group; and m is 1, 2, or 3, preferably 1. Specific examples of said amides are mono-ethanol amine coconut fatty acid amide and diethanol amine dodecyl fatty acid amide. These acyl moieties may be derived from naturally occurring glycerides, e.g., coconut oil, palm oil,

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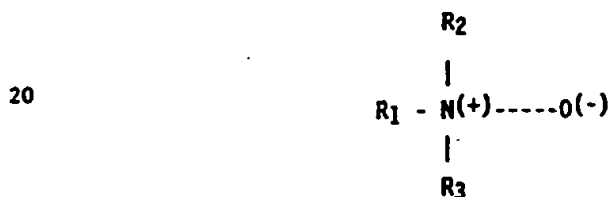
soybean oil, and tallow, but can be derived synthetically, e.g., by the oxidation of petroleum or by hydrogenation of carbon monoxide by the Fischer-Tropsch process. The monoethanol amides and diethanolamides of C₁₂₋₁₄ fatty acids are preferred.

5 Amine oxide semi-polar nonionic surfactants comprise compounds and mixtures of compounds having the formula:



wherein R₁ is an alkyl, 2-hydroxyalkyl, 3-hydroxyalkyl, or 3-alkoxy-2-hydroxypropyl radical in which the alkyl and alkoxy, respectively, contain from about 8 to about 18 carbon atoms, R₂ and R₃ are each methyl, ethyl, propyl, isopropyl, 2-hydroxyethyl, 2-hydroxypropyl, or 3-hydroxypropyl, and n is from 0 to about 10. Particularly preferred are amine oxides of the formula:

15



wherein R₁ is a C₁₂₋₁₆ alkyl and R₂ and R₃ are methyl or ethyl. The above ethylene oxide condensates, amides, and amine oxides are more fully described in U.S. Pat. No. 4,316,824 (Pancheri), incorporated herein by reference.

25

The composition of this invention can also contain certain cationic quarternary ammonium surfactants of the formula:



or amine surfactants of the formula:



wherein R¹ is an alkyl or alkyl benzyl group having from about 6 to about 16 carbon atoms in the alkyl chain; each R² is selected from the group consisting of -CH₂CH₂-, -CH₂CH(CH₃)-, -CH₂CH(CH₂OH)-, -CH₂CH₂CH₂-, and mixtures thereof; each R³ is selected from the group consisting of C₁-C₄ alkyl, C₁-C₄

- 19 -

hydroxyalkyl, benzyl, and hydrogen when y is not 0; R⁴ is the same as R³ or is an alkyl chain wherein the total number of carbon atoms of R¹ plus R⁴ is from about 8 to about 16; each y is from 0 to about 10, and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Preferred of the above are the alkyl quaternary ammonium surfactants, especially the mono-long chain alkyl surfactants described in the above formula when R⁴ is selected from the same groups as R³. The most preferred quaternary ammonium surfactants are the chloride, bromide, and methylsulfate C₈-16 alkyl trimethylammonium salts, the C₈-16 alkyl di(hydroxyethyl)methylammonium salts, the C₈-16 alkyl hydroxyethyldimethylammonium salts, C₈-16 alkyloxypropyl trimethylammonium salts, and the C₈-16 alkyloxypropyl dihydroxyethylmethylammonium salts. Of the above, the C₁₀-14 alkyl trimethylammonium salts are preferred, e.g., decyl trimethylammonium methylsulfate, lauryl trimethylammonium chloride, myristyl trimethylammonium bromide and coconut trimethylammonium chloride, and methylsulfate.

The suds boosters used in the compositions of this invention can contain any one or mixture of the suds boosters listed above.

Additional Optional Ingredients

In addition to the ingredients described hereinbefore, the compositions can contain other conventional ingredients suitable for use in liquid or gel dishwashing compositions.

Magnesium ions may be added to the composition in amounts from 0.01% to about 4%, preferably from about 0.1% to about 3% and added as chloride, acetate, formate or nitrate, preferably a chloride or formate, salt.

Optional ingredients include drainage promoting ethoxylated nonionic surfactants of the type disclosed in U.S. Pat. No. 4,316,824, Pancheri (February 23, 1982), incorporated herein by reference.

Alcohols, such as C₁-C₄ monohydric alcohol, preferably ethyl alcohol and propylene glycol, can be utilized in the interests of achieving a desired product phase stability and viscosity. Alcohols such as ethyl alcohol and propylene glycol at a level of

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from 0% to about 15%, more preferably from about 0.1% to about 10% by weight of the composition are particularly useful in the liquid compositions of the invention.

5 Gel compositions of the invention normally would not contain alcohols. These gel compositions may contain urea and conventional thickeners at levels from about 10% to about 30% by weight of the composition as gelling agents.

10 Other desirable ingredients include diluents and solvents. Diluents can be inorganic salts, such as ammonium chloride, sodium chloride, potassium chloride, etc.; and the solvents include water, lower molecular weight alcohols, such as ethyl alcohol, isopropyl alcohol, etc.

FORMULATION

15 Generally, any convention process may be employed in formulating the compositions of the present invention. However, the order of disulfonate surfactant addition may be important in formulating a stable concentrated light duty liquid diswashing detergent composition of the present invention. It has been seen that the disulfonate surfactant should be added to the surfactant
20 paste of the composition.

Method Aspect

25 In the method aspect of this invention, soiled dishes are contacted with an effective amount, typically from about 0.5 ml. to about 20 ml. (per 25 dishes being treated), preferably from about 3 ml. to about 10 ml., of the detergent composition of the present invention. The actual amount of liquid detergent composition used will be based on the judgement of user, and will typically depend upon factors such as the particular product formulation of the composition, including the concentration of
30 active ingredient in the composition, the number of soiled dishes to be cleaned, the degree of soiling on the dishes, and the like. The particular product formulation, in turn, will depend upon a number of factors, such as the intended market (i.e., U.S., Europe, Japan, etc.) for the composition product. The following
35 are examples of typical methods in which the detergent compositions of the present invention may be used to clean dishes.

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These examples are for illustrative purposes and are not intended to be limiting.

5 In a typical U.S. application, from about 3 ml. to about 15 ml., preferably from about 5 ml. to about 10 ml. of a liquid detergent composition is combined with from about 1,000 ml. to about 10,000 ml., more typically from about 3,000 ml. to about 5,000 ml. of water in a sink having a volumetric capacity in the range of from about 5,000 ml. to about 20,000 ml., more typically from about 10,000 ml. to about 15,000 ml. The detergent
10 composition has a surfactant mixture concentration of from about 21% to about 44% by weight, preferably from about 25% to about 40% by weight. The soiled dishes are immersed in the sink containing the detergent composition and water, where they are cleaned by contacting the soiled surface of the dish with a cloth, sponge, or
15 similar article. The cloth, sponge, or similar article may be immersed in the detergent composition and water mixture prior to being contacted with the dish surface, and is typically contacted with the dish surface for a period of time ranging from about 1 to about 10 seconds, although the actual time will vary with each
20 application and user. The contacting of the cloth, sponge, or similar article to the dish surface is preferably accompanied by a concurrent scrubbing of the dish surface.

25 In a typical European market application, from about 3 ml. to about 15 ml., preferably from about 3 ml. to about 10 ml. of a liquid detergent composition is combined with from about 1,000 ml. to about 10,000 ml., more typically from about 3,000 ml. to about 5,000 ml. of water in a sink having a volumetric capacity in the range of from about 5,000 ml. to about 20,000 ml., more typically from about 10,000 ml. to about 15,000 ml. The detergent
30 composition has a surfactant mixture concentration of from about 20% to about 50% by weight, preferably from about 30% to about 40%, by weight. The soiled dishes are immersed in the sink containing the detergent composition and water, where they are cleaned by contacting the soiled surface of the dish with a cloth, sponge, or similar article. The cloth, sponge, or similar article
35 may be immersed in the detergent composition and water mixture prior to being contacted with the dish surface, and is typically

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contacted with the dish surface for a period of time ranging from about 1 to about 10 seconds, although the actual time will vary with each application and user. The contacting of the cloth, sponge, or similar article to the dish surface is preferably accompanied by a concurrent scrubbing of the dish surface.

5 In a typical Latin American and Japanese market application, from about 1 ml. to about 50 ml., preferably from about 2 ml. to about 10 ml. of a detergent composition is combined with from about 50 ml. to about 2,000 ml., more typically from about 100 ml. 10 to about 1,000 ml. of water in a bowl having a volumetric capacity in the range of from about 500 ml. to about 5,000 ml., more typically from about 500 ml. to about 2,000 ml. The detergent composition has a surfactant mixture concentration of from about 5% to about 40% by weight, preferably from about 10% to about 30% 15 by weight. The soiled dishes are cleaned by contacting the soiled surface of the dish with a cloth, sponge, or similar article. The cloth, sponge, or similar article may be immersed in the detergent composition and water mixture prior to being contacted with the dish surface, and is typically contacted with the dish surface for 20 a period of time ranging from about 1 to about 10 seconds, although the actual time will vary with each application and user. The contacting of the cloth, sponge, or similar article to the dish surface is preferably accompanied by a concurrent scrubbing of the dish surface.

25 Another method of use will comprise immersing the soiled dishes into a water bath without any liquid dishwashing detergent. A device for absorbing liquid dishwashing detergent, such as a sponge, is placed directly into a separate quantity of undiluted liquid dishwashing composition for a period of time typically 30 ranging from about 1 to about 5 seconds. The absorbing device, and consequently the undiluted liquid dishwashing composition, is then contacted individually to the surface of each of the soiled dishes to remove said soiling. The absorbing device is typically contacted with each dish surface for a period of time range from 35 about 1 to about 10 seconds, although the actual time of application will be dependent upon factors such as the degree of soiling

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of the dish. The contacting of the absorbing device to the dish surface is preferably accompanied by concurrent scrubbing.

As used herein, all percentages, parts, and ratios are by weight unless otherwise stated.

5 The following Examples illustrate the invention and facilitate its understanding.

EXAMPLE I

10 The following concentrated light duty liquid compositions are prepared as follows:

Table 1

		<u>% By Weight</u>		
<u>Ingredients</u>		<u>A</u>	<u>B</u>	<u>C</u>
	Sodium xylene sulfonate	3.00	3.00	0.00
15	Diethylenetriamine penta acetate	0.06	0.06	0.06
	Ethanol	8.06	8.06	8.06
	Propylene glycol	1.60	1.60	1.60
	Magnesium chloride	3.21	3.21	3.21
	Sodium alkyl ethoxy(1.0) sulfate	9.00	9.00	9.00
20	Sodium alkyl ethoxy(3.0) sulfate	19.80	19.80	19.80
	Polyhydroxy fatty acid amide	9.00	9.00	9.00
	Amine oxide	3.00	3.00	3.00
	NEODOL® 1-91	3.15	3.15	3.15
	Perfume	0.09	0.09	0.09
25	DOWFAX 2A1	0.00	0.00	1.35
	Calcium formate	0.00	1.33	0.00
	Calcium chloride dihydrate	1.51	0.00	1.51
	Water	-----	Balance	-----

30 1 C₁₁E₉ nonionic surfactant

Stability is assessed by placing the products in a 120°F environment for one week. Results are as follows.

Table 2

<u>Stability</u>		<u>A</u>	<u>B</u>	<u>C</u>
35	120°F/1 month	precipitate	precipitate	clear

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Composition C containing a disulphonate surfactant (DOWFAX 2A1) remains stable in a harsher environment than those concentrated compositions which do not contain the surfactant.

EXAMPLE II

The following light duty liquid compositions are prepared as follows:

Table 3

		<u>% By Weight</u>			
	<u>Ingredients</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>
10	Sodium xylene sulfonate	2.30	2.30	1.15	0.00
	Diethylenetriamine penta acetate	0.06	0.06	0.06	0.06
	Ethanol	9.15	9.15	9.15	9.15
	Magnesium hydroxide	2.18	2.18	2.18	2.18
15	Sucrose	1.50	1.50	1.50	1.50
	Alkyl ethoxy(1.0) sulfate	34.14	34.14	34.14	34.14
	Sodium hydroxide	1.13	1.13	1.13	1.13
	Polyhydroxy fatty acid amide	6.50	6.50	6.50	6.50
	Amine oxide	3.00	3.00	3.00	3.00
20	Cocoamidopropyl betaine	2.00	2.00	2.00	2.00
	Perfume	0.23	0.23	0.23	0.23
	DOWFAX 2A1	0.00	0.00	0.00	0.00
	Calcium xylene sulfonate	0.00	0.00	3.59	3.58
	DOWFAX 3B2	0.00	0.00	1.15	1.15
25	Calcium formate	0.00	1.14	0.00	0.00
	Calcium chloride dihydrate	1.28	0.00	0.00	0.00
	Water	-----Balance-----			

		<u>% By Weight</u>	
	<u>Ingredients</u>	<u>H</u>	<u>I</u>
30	Sodium xylene sulfonate	0.00	0.00
	Diethylenetriamine penta acetate	0.06	0.06
	Ethanol	9.15	9.15
	Magnesium hydroxide	2.18	2.18
35	Sucrose	1.50	1.50
	Alkyl ethoxy(1.0) sulfate	34.14	34.14
	Sodium hydroxide	1.13	1.13

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	Polyhydroxy fatty acid amide	6.50	6.50
	Amine oxide	3.00	3.00
	Cocoamidopropyl betaine	2.00	2.00
	Perfume	0.23	0.23
5	DOWFAX 2A1	1.04	2.30
	Calcium xylene sulfonate	0.00	0.00
	DOWFAX 3B2	0.00	0.00
	Calcium formate	0.00	1.14
	Calcium chloride dihydrate	1.28	0.00
10	Water	----Balance---	

Stability is assessed by placing the products in 120°F environment for one week and visually assessing appearance. Results are as follows.

15

Table 4

<u>Stability</u>	D	E	F	G
120°F/1 week	precipitate	precipitate	clear	clear
<u>Stability</u>	H	I		
120°F/1 week	clear	clear		

20

Compositions containing disulfonate surfactants (Compositions F and G, DOWFAX 3B2, and Compositions H and I, DOWFAX 2A1) are more stable at harsher temperatures than those compositions containing sodium xylene sulfonate alone (Compositions D and E).

25

EXAMPLE III

The following light duty liquid compositions are prepared as follows:

30

Table 5% By Weight

35

<u>Ingredients</u>	H	I
Alkyl dimethyl betaine	2.00	0.00
Cocoamidopropyl betaine	0.00	2.00
Diethylenetriamine penta acetate	0.06	0.06
Ethanol	7.00	10.00
Sodium alkyl ethoxy(1.0) sulfate	15.00	20.00
Magnesium chloride (2.6) HOH	2.35	4.91

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	Alkyl ethoxy(3.5) carboxylate	3.79	0.00
	Sodium alkyl ethoxy(3.0) sulfate	6.00	6.00
	Polyhydroxy fatty acid amide	6.00	6.00
	Amine oxide	1.00	1.50
5	NEODOL® 1-91	10.00	10.00
	Sodium cumene sulfonate	2.00	2.00
	2-butyl-1-octanoic acid	4.00	5.00
	Alkyl diphenyl oxide disulfonate ²	4.00	4.00
	Perfume	0.15	0.18
10	Tetronic®	0.00	0.10
	Hydrogen chloride	0.00	0.18
	Water and trim	---	Balance ---
	pH	8.3	8.3

- 15 ¹ C9E11 nonionic surfactant
 ² DOWFAX® 2A1

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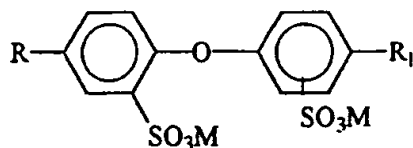
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What is Claimed is:

1. A liquid or gel detergent composition comprising, by weight of the composition:
 - 5 (a) from 20% to 95% of a surfactant selected from the group consisting of anionic surfactant, nonionic surfactant, amphoteric surfactant, and mixtures thereof;
 - (b) from 0.01% to 4.0% of calcium ions; said calcium ions preferably added to said composition as a salt selected from the group consisting of chloride, acetate, nitrate, formate, xylene sulfonate and mixtures thereof;
 - 10 (c) from 0.5% to 40% disulfonate surfactant;
 - (c) from 5.0% to 45% of water;wherein said composition has a pH in a 10% solution in water at 20°C of between 7 and 10.
- 15 2. A composition according to Claim 1 comprising from 30% to 75% surfactant selected from the group consisting of alkyl sulfate; alkyl ether sulfate; polyethercarboxylate; secondary olefin sulfonates; sarcosinates; methyl ester sulphonates; alkylglycerol ether sulphonate; polyethylene; polypropylene and polybutylene oxide condensate of alkyl phenols; alkyl ethoxylate condensation
20 products of aliphatic alcohols with ethylene oxide; the condensation products of ethylene oxide with a hydrophobic base formed by condensation of propylene oxide with proylene glycol; condensation product of ethylene oxide and ethylenediamine; alkypolysaccharides; fatty acid amides; alkyl ethoxy carboxylates; special soaps; polyhydroxy fatty acid amides and mixtures thereof.
- 25 3. A composition according to Claim 1 or 2 further comprising from 0.1% to 5% sugar selected from the group consisting of sucrose, maltose (malt sugar), cellobiose, lactulose, lactose, gluconic acid, glucose, fructose, galactose; xylose, ribose and mixtures thereof.
- 30 4. A composition according to any one of the preceding claims wherein said disulfonate surfactant is an alkyl diphenyl oxide disulfonate surfactant of the general formula:

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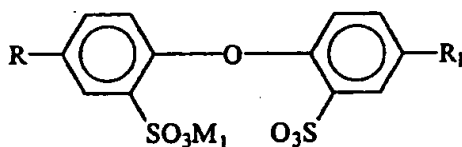


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R = C10-C18, may be branched or linear

R₁ = H or R

M = Na⁺, K⁺, NH₄⁺, CA⁺⁺, or Mg⁺⁺; or



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R = C10-C18, may be branched or linear

R₁ = H or R

M₁ = CA⁺⁺ or Mg⁺⁺

45 5. A composition according to any one of the preceding claims comprising from 0.1% to 2% calcium ions.

6. A composition according to any one of the preceding claims further comprising less than 15% of a suds booster selected from the group consisting of betaines, sultaines, complex betaines, ethylene oxide condensates, fatty acid amides, amine
50 oxide semi-polar nonionics, cationic surfactants, and mixtures thereof.

7. A composition according to any one of the preceding claims comprising from 0.05% to 4.0% sugar.

55

8. A light duty liquid dishwashing detergent composition comprising by weight:

- a) from 40% to 70% surfactant selected from the group consisting of anionic surfactants, nonionic surfactants, amphoteric surfactants and mixtures thereof;
- b) from 0.1% to 2.0% calcium ions added as a salt selected from the group
60 consisting of xylene sulfonate, formate, chloride and mixtures thereof;
- c) from 0.5% to 25% alkyl diphenyl oxide disulfonate;

- d) from 0.5% to 4.0% sugar selected from the group consisting of sucrose, maltose (malt sugar), lactose, gluconic acid, glucose, fructose, and mixtures thereof,
- 65 e) from 0.1% to 3% magnesium added as a salt selected from the group consisting of chloride, formate and mixtures thereof; and
- f) from 0.5 to 12% of a suds booster selected from the group consisting of betaines, fatty acid amides, amine oxide semi-polar nonionics, and mixtures thereof,
- 70 wherein said composition has a pH in a 10% solution in water at 20°C of between 7 and 9.0.

9. A composition according to any one of the preceding claims wherein said surfactant is selected from the group consisting of alkyl ethoxy carboxylates, polyhydroxy fatty acid amides, alkyl ether sulfates and mixtures thereof.

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10. A method for providing stable concentrated compositions which comprises adding disulfonate surfactant to one or more anionic surfactant, nonionic surfactant, amphoteric surfactant or mixtures thereof, and calcium ions, wherein said disulfonate surfactant is an alkyl diphenyl oxide surfactant.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 94/08947

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D17/00 C11D1/24 C11D3/34 C11D3/22 C11D1/94
C11D1/86 C11D1/83 C11D1/65

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,92 08777 (THE PROCTER & GAMBLE CO.) 29 May 1992 see the whole document ----	1,2,5,6, 8,9
A	WO,A,92 06171 (THE PROCTER & GAMBLE CO.) 16 April 1992 see the whole document ----	1,2,5,6, 8,9
A	GB,A,2 058 823 (UNILEVER) 15 April 1981 see the whole document ----	1,2,6,8, 9
A	GB,A,2 078 246 (THE PROCTER & GAMBLE CO.) 6 January 1982 see the whole document ----	1,2,6,8, 9
-/-		

☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

12 January 1995

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Serbetsoglou, A

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 94/08947

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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